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A NANO SILVER REPLACEMENT FOR HIGH LEAD SOLDERS IN SEMICONDUCTOR JUNCTIONS

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ABSTRACT

While it is now widely accepted that most electronic assembly can be reliably effected with lead-free solders, a practicable alternative to the high-lead high-melting-point solders has not been available. That reality has been acknowledged by the interim exemption from the requirements of the EU RoHS Directive granted for solders with 85% or more of lead. With no direct replacement yet found by conventional alloying of elements permitted by the RoHS Directive the search for a replacement for these high-lead solders has extended to alternative joining materials. One approach has been to take advantage of the reactivity of nano particles of silver to make a product that while ultimately having a melting point at or near the silver melting point of 961.8°C can combine to form reliable connections at temperatures much lower than that. The challenge in this approach is that the very reactivity that makes the formation of a joint possible at a relatively low temperature means that the nano silver tends to be unstable. In this paper the authors report the development of a unique nano silver material that is manufactured and stabilized in an alcohol environment to produce a material that can be used to make reliable joints between a wide range of the substrates commonly used in electronics in process conditions similar to those used with high-lead solders. This material can be used to make joints to ferrous materials (e.g. stainless steel) as well as non-ferrous materials such as copper and nickel. And most importantly for component manufacture this new material bonds strongly to semiconductor materials such as silicon. Where even longer life in thermal cycling is required the silver structure can be reinforced by the addition of other materials in the form of particles of the appropriate size. The paper will include details of mechanical and reliability testing of joints made with these materials under a range of temperature, pressure and atmosphere conditions.

Key words: Nano Silver, die attach

INTRODUCTION

The main application for high- Pb solders that resulted in the granting of an exemption from the requirement of the EU RoHS Directive has been in semiconductor packaging. The relatively high melting point of these solders (around 300°C) means that joints made with them in earlier stages of component assembly are not disturbed by subsequent stages of assembly with lower melting solders (step soldering) or by the high peak temperature sometimes required in final reflow soldering.

For power semiconductors the die-attach material has to be able to maintain a reliable joint at the relatively high operating temperature of these devices while at the same time providing a high thermal conductivity path for dissipation of the heat generated during their operation.

In this application the trend to wide bandgap semiconductor devices such as SiC power diodes and transistors means that there is an advantage if the die-attach material can sustain a higher operating temperature than can the high-Pb solders. With SiC devices a substantial increase in power density can be achieved because of its higher thermal conductivity, higher breakdown voltage and higher saturated carrier velocity. The larger bandgap of SiC can allow higher junction temperatures without compromising performance. [1]

The conventional metallurgical alternatives to the high-lead solders such as the gold-tin eutectic have a processing temperature that is higher than the semiconductor can tolerate without degradation, And another alternative, silver-filled epoxy cannot always provide the thermal conductivity that is required to keep the die at a temperature at which it can operate at maximum efficiency [1] [2].

The relatively high surface activity of nano particles means that, for example a 2.4nm Silver particle would be expected to have a melting point of 350°C [3], much less than the 961.8°C melting point of bulk silver (Figure 1). The outer layers of such a particle would have a mobility similar to that of the molten state at even lower temperatures so that they will bond to each other or to other compatible materials by wetting and interdiffusion at temperatures well below those required for conventional sintering of conventional Silver powder.

Although the application of external pressure during the sintering process does increase the area of contact of the particles it is not essential in sintering nano silver particles. Even at temperatures less than those used in reflowing the high-lead solders the capillary forces generated by the mobile atoms at the surface of the silver are sufficient to ensure the wetting of adjacent particles with which they are in contact. Since silver is so much stronger than solder the full density of silver is not required to achieve the strength required in this application. In fact the lower modulus of the porous structure is an advantage in reducing the stress generated in the chip during thermal cycling because of the differences in the coefficient of thermal expansion

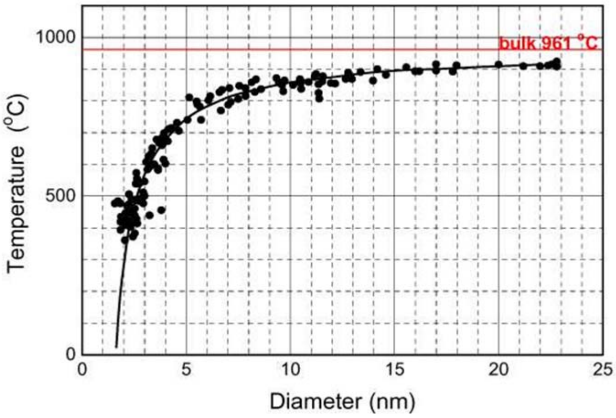


Figure 1. Silver melting point as a function of particle size [4]

When properly formulated, pastes based on nano particles of silver can be processed to form reliable joints at temperatures that fall within a range similar to that required for the high-Pb solders and even lower.

NANO SILVER

There are significant challenges to be faced in delivering the highly reactive nano silver particles to the joint area and then facilitating their bonding to form a structurally strong joint that delivers the required levels of electrical and thermal conductivity.

Manufacturing the nano silver particles in itself is a major challenge but if they are to remain as nano particles with the properties required for them to sinter at the lowest possible temperature they have to be stabilized until they are in place in the joint gap ready for sintering. That is achieved by passivating or capping the particle during the manufacturing process with a coating that bonds to the nano silver surface while presenting a resistant external surface.

Chemicals such as thiols, amines and carboxylates have been identified as effective capping materials [2] but these are bound strongly to the silver and require a high temperature for their removal, to some extent negating the chief advantage of the nano particles they are protecting. Some capping materials require sintering to occur in air so that they can be removed by oxidation and that can compromise other parts of the component that need the protection of a nitrogen atmosphere at sintering temperatures.

Another disadvantage of some of these capping agents is residues of sulphur and nitrogen compounds that can interfere with the performance of the sintered silver and contribute to corrosion problems in service.

There is thus a strong motivation to identify a capping material that would not suffer from these disadvantages and make possible wider application of nano-silver bonding as a reliable die-attach material.

For practical application in commercial mass production the nano-silver bonding materials must also have the physical properties required by the application process, which might be screen printing, dispensing or dipping. This is achieved by dispersing the capped nano- silver particle in a suitable vehicle. The rheology can also be optimised by the inclusion in the mix of sub-micron particles of silver or other metals such as Cu and by adjustment of the particle size distribution

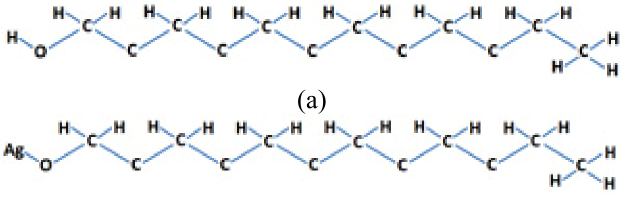
While offering the possibility of relatively low process temperatures and high temperature reliability, silver suffers from the disadvantage of a relatively high elastic modulus so that potentially damaging levels of stress can be developed in the die by the strains arising from CTE differences during the thermal cycling that can occur in service. Another objective in optimizing nano silver bonding materials is, therefore, the control of the microstructure to minimise the elastic modulus while retaining a high level of thermal conductivity.

ALCOXIDE-PASSIVATED NANO SILVER

In an attempt to address the problems encountered with established nano silver capping materials the possibility of using alcohols was explored. These can attach to the silver through the formation of alcoxides with silver atoms on the surface of the nano particle. The advantage of these chemicals in this application is that the oxygen-silver bond, while strong enough to stabilize the nano particle during manufacturing processes and subsequent storage and handling, is weak enough that it can be broken at a relatively low temperature to expose the active surface of the nano particle so that it can bond to adjacent particles. This opens the way to nano-silver materials that can effect bonding with thermal profiles comparable with those used for reflow soldering.

For example, alcoxide-capped nano silver particles were produced by reacting silver carbonate (Ag_2CO_3) with n-dodecanol ($CH_3(CH_2)_{11}OH$) or n-decanol ($CH_3(CH_2)_9OH$) under a nitrogen atmosphere. In this reaction the hydrogen atom (H) in the hydroxyl group at the end of n-dodecanol or n-decanol molecule (Figure 2 (a)) is replaced by a silver atom on the surface of the nano particle as it forms by reduction of the silver carbonate (Figure 2(b)) [5]

The result, a nano silver particle, protected by the n-dodecanoxide molecules, is illustrated schematically in Figure 3.



(a)

(b)

Figure 2. n-dodecanol (a) and Ag n-dodecanoxide (b)

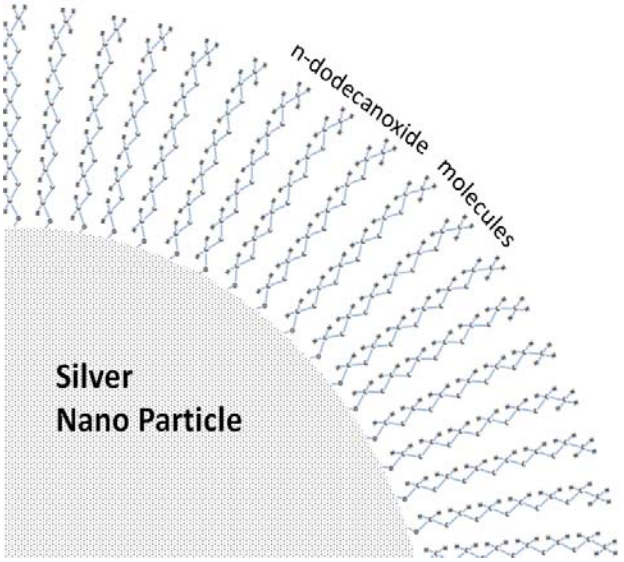


Figure 3. Schematic representation of alcoxide-passivated nano silver particle.

The resulting mixture was cooled and the stabilized nano-silver particles filtered out washed in ethanol, dried and dispersed in hexane. The nature of the material so produced was confirmed by placing some of this dispersion on a carbon film substrate for examination in a transmission electron microscope (TEM).

The particles were observed to be roughly spherical with a diameter of <5nm (Figure 4). The lattice planes of these crystalline particles is apparent in the TEM image and the estimated 0.23nm spacing between planes is consistent with the spacing of the [111] plane of silver's close packed cubic crystal structure.

The arrangement of the nano-silver particles on the carbon film in an approximately hexagonal pattern (Figure 5) suggests that in that area they are close packed so that their separation distance is determined by the thickness of the protective alcoxide coating. The estimated gap between the nano-silver cores of these particles of 2.5nm is close to the expected length of two n-dodecanoxide molecules aligned end to end, which is consistent with the passivation model illustrated schematically in Figure 3.

Similar reactions can be effected with shorter alcohols but as the number of carbon atoms in the alcohol falls the size of the nano particle produced increases (Figure 6).

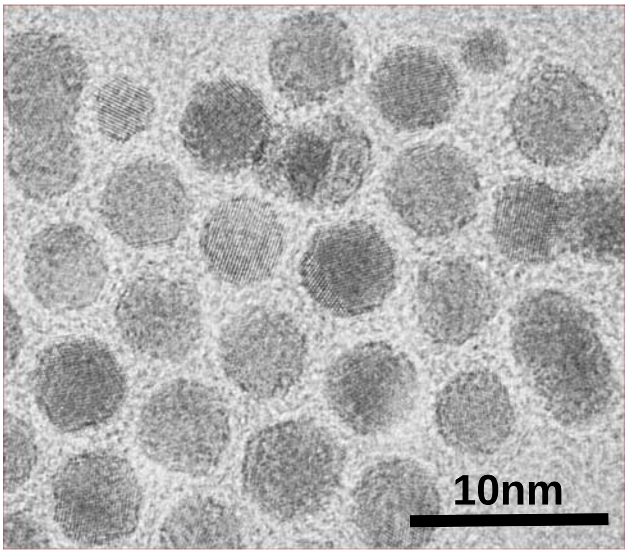


Figure 4. Dodecanoxide-passivated nano-silver particles recovered from reaction with Ag2CO3.

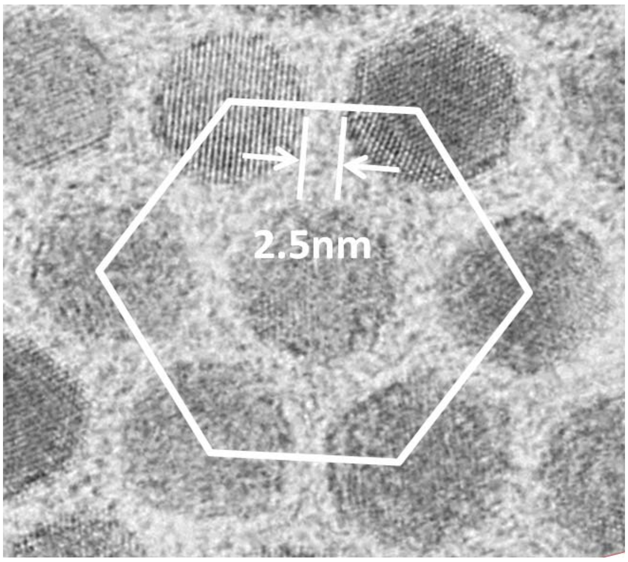


Figure 5. Close-packed arrangement of nano-silver particles with spacing approximately twice the length of the passivating n-dodecanol molecule

SINTERING NANO SILVER

Nano-silver particles were mixed with 0.4µm silver powder in an isobonyl cyclohexanol (IBCH) vehicle to achieve a total metal content of 87% with the dodecanoxide-passivated nano-silver. This mixture was subjected to thermogravimetric and differential thermal analysis in air and nitrogen atmospheres with the temperature being raised at the rate of 10°C/minute.

The stages in the sintering process are apparent in Figure 7. The first stage is evaporation of the carrier and removal of the passivation layer. In air there is a highly exothermic reaction as the passivating alcohol is oxidized but in a nitrogen atmosphere the alcohol simple detaches with little heat evolution. With the passivation layer removed the active surface of the nano silver particles is exposed and the sintering proceeds.

The temperature at which sintering occurs varies with the number of carbon atoms in the passivating alcoxide molecule and it can be seen in Figure 8 that sintering can be effected at temperatures under 120°C nano silver passivated with alcoxides with 2-6 carbon atoms. There is, however, a trade off in that the passivation by these shorter alcoxide molecules is not as stable as that of the longer molecules.

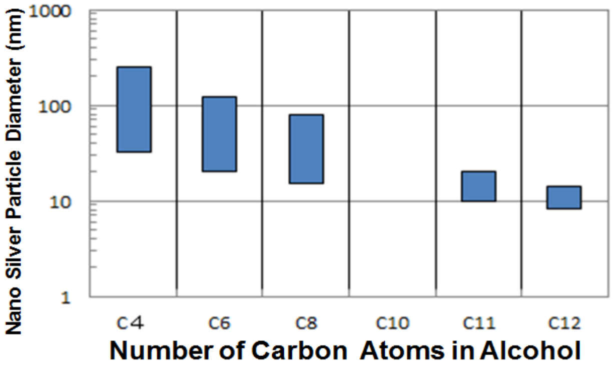


Figure 6. Relationship between the size of the silver nano particle and the alcohol used in its manufacture.

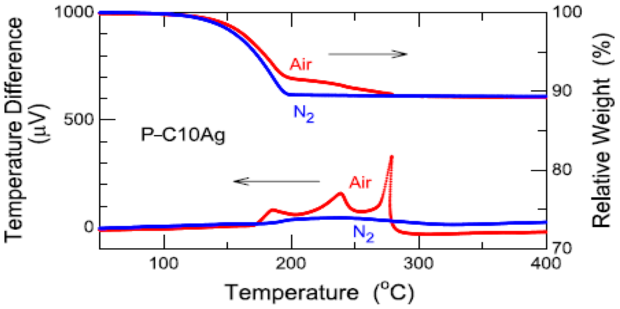


Figure 7. TGA-DTA plots for decanoxide-passivated nano-silver and 5µm silver mixtures dispersed in IBCH.

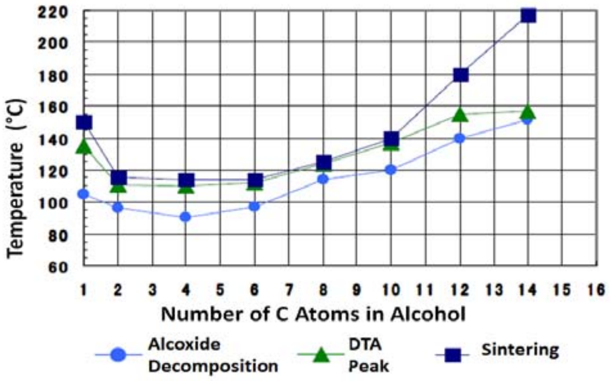


Figure 8. Sintering behaviour as a function of alcoxide passivator.

OPTIMIZING THE NANO SILVER PASTE

While it is possible to form a joint by sintering pure nano-particles there are cost and performance advantages to be achieved by mixing nano particles with conventional particles to which the nano particles can also bond at low temperatures. This arrangement is illustrated schematically in Figure 9.

The idea is to use a range of particle sizes that when bonded will fill the volume to the level required to achieve the required mechanical, electrical and thermal properties. The sub-micron voids in the sintered paste (Figure10) mean that the bond is more compliant than if it were solid silver so that the stress imposed on the die during thermal excursions due to CTE differences can be at least partly accommodated. However, the electrical and thermal conductivity of the sintered bond are still adequate.

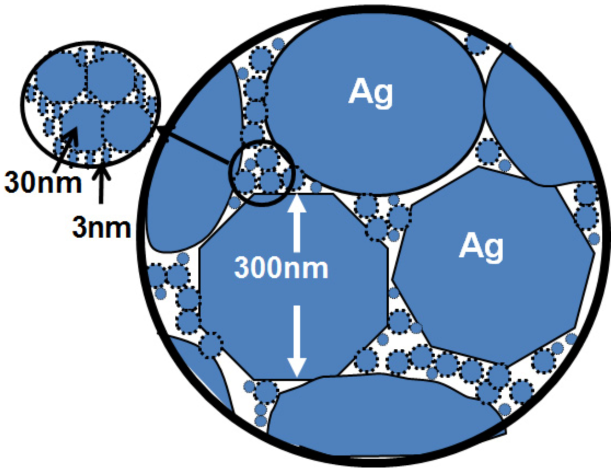


Figure 9. Schematic representation of a typical mix of nano silver particles with larger silver particles

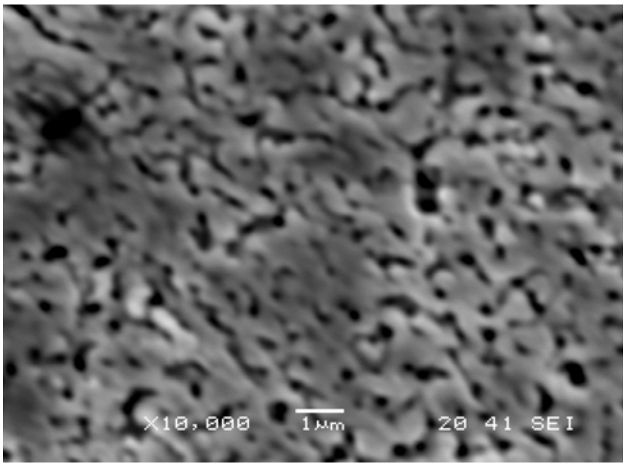


Figure 10. Submicron voids in sintered alcoxide-passivated nano silver

PROPERTIES OF SINTERED NANO SILVER

The electrical conductivity of the sintered silver was assessed by printing a film of paste onto glass and measuring its resistance using the four terminal method. The data summarized in Figure 11 indicates that resistance varies in the range 2-15μΩcm, which is generally greater than the 1.6μΩ resistivity of bulk silver but at least as good as the resistivity of reflowed Pb-5Sn solder paste and better than the resistivity of silver/epoxy paste.

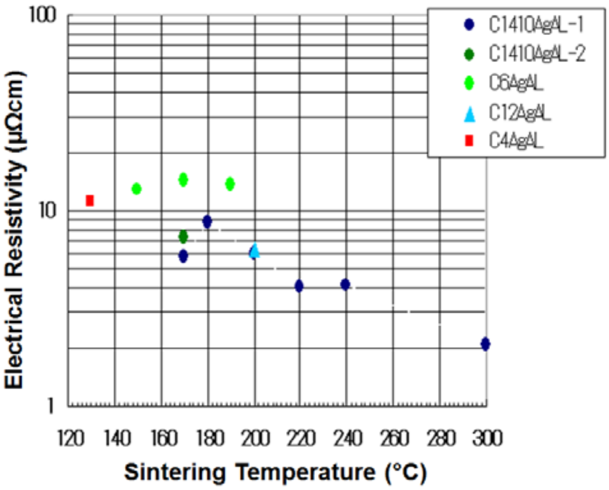


Figure 11. Electrical resistivity of nano silver paste as a function of sintering temperature. Sintering temperature varies with the number of carbon atoms in the passivating alcoxide.

AN EVALUATION

As a test of the practical applicability of pastes based on this nano silver technology a silicon diode package such as that represented in schematically in Figure 12 was assembled. The finish on the 2.3mm x 2.3mm x 0.25mm diode chip was gold and the substrate copper.

In the nitrogen atmosphere the assembly was heated to 300°C, a temperature similar to that which would be required to reflow the high-lead solder paste normally used in the manufacture of this product. In air the temperature was raised to 350°C to allow for burning off of the passivating material. The total time of the sintering process was 25 minutes in the nitrogen atmosphere and 30 minutes in air. No pressure was applied to the joint during the sintering process. After the joint was effected the components were packaging in resin according to normal production practice.

The stability of the electrical and thermal resistance of the joint was assessed by exposing the package to thermal cycling -55°C to 150°C. The results are plotted in Figure 13.

The electrical resistance was taken to be indicated by the forward voltage V_F at a constant current of 3A. Thermal resistance was estimated by measuring the difference in V_F before and after Joule heating with 100ms pulse of 10A.

In the as-manufactured condition diodes assembled with pastes based on nano silver passivated with both dodecanoxide and decanoxide had electrical and thermal resistances similar to those of that assembled with high-lead solder paste. The electrical resistance of those assembled with nano silver in air suffered rapid increase in electrical resistance. The increase in resistance of the diodes assembled with nano silver paste and sintered in nitrogen was similar to that of the diodes assembled with high-lead solder paste.

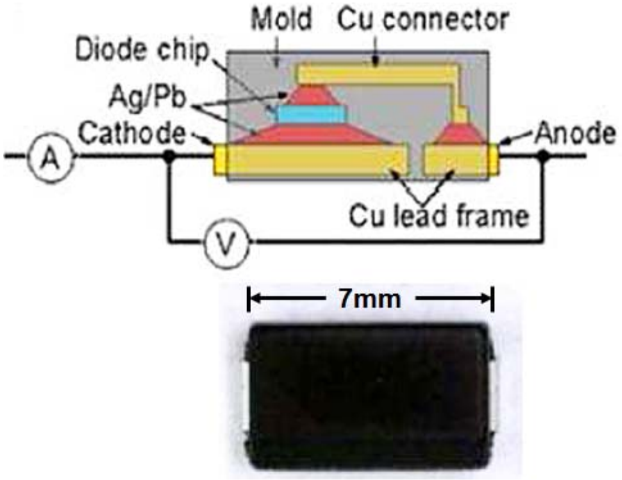


Figure 12. Nano-silver evaluation package

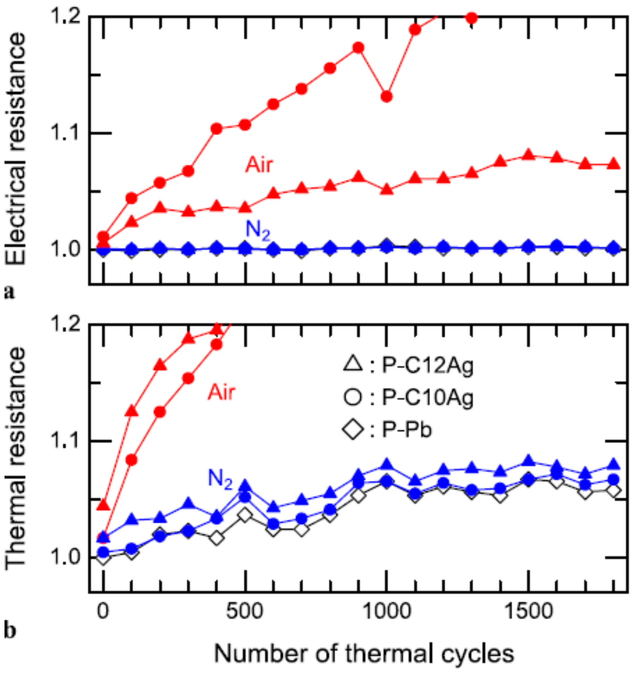


Figure 13. Electrical and thermal resistance of silicon diode package sintered in air and nitrogen as a function of the number of thermal cycles of -55°C-150°C. Results are normalized to that of the diode assembled with high-lead solder paste as manufactured. In the product code C12 and C10 indicate the number of carbon atoms in the passivating alcohol

While the thermal resistance of the diode assembled with high-lead solder paste or nano silver pasted sintered in nitrogen remained stable, that of the diodes assembled with nano silver paste passivated with dodecanol and deconal pastes sintered in air suffered significant loss of conductivity. Further investigation is required but it is presumed that the lower stability of joints sintered in air is a consequence of oxidation of the silver. An advantage of the alcoxide passivation is that oxygen is not required in its removal during the sintering process so that the process can be carried out in a nitrogen atmosphere. Simple breakdown of the alcoxide bond is sufficient to allow the sintering process to proceed.

Metallographic examination of a cross-section through the joint to the copper substrate effected by the nano silver paste indicates that it differs from that formed by the high-lead solder paste in that there is no intermetallic layer at the interface. The silver is bonded directly the copper substrate (Figure 14).

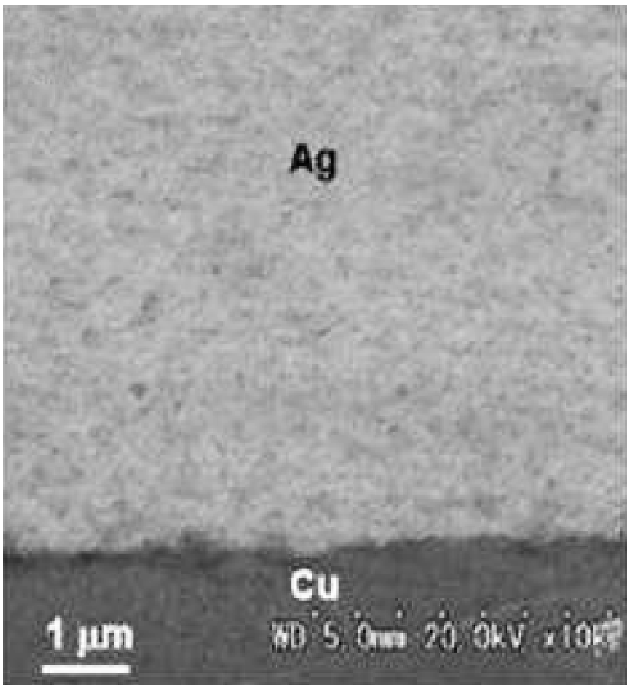


Figure 14. The bond line between the copper substrate and the sintered nano silver paste.

MECHANICAL PROPERTIES

Shear testing indicated the greater strength of joints made to copper with the the sintered alcoxide-passivated paste compared with those made with reflowed Pb-5Sn solder paste (Figure 15).

Although the shear strength of joints was greater when 1MPa of pressure was applied to the shear test piece during sintering the strength of joints made with the alcoxide-passivated nano silver paste exceeded that of a reflowed Pb-5Sn joint (Figure 17) even when the paste was sintered without applied pressure.

As explained earlier the sintering temperature can be adjusted by selecting the number of carbon atoms in the alcohol used. The results of shear testing joints made between copper surfaces with nano silver material fired at low, medium and high temperatures indicates that although those sintered at high temperature are stronger, even those sintered at lower temperatures are at least comparable in strength to joints made with reflowed Pb-5Sn solder.

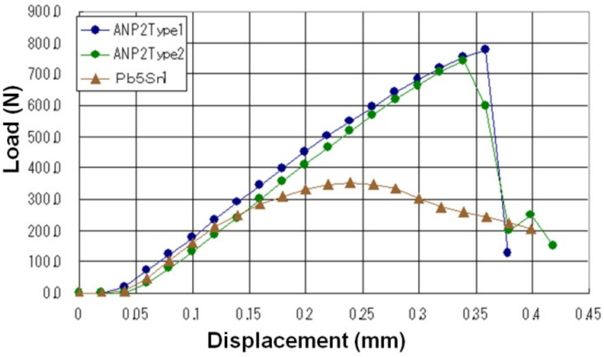


Figure 15. Shear testing load-displacement plots for sintered alcoxide-passivated nano silver joints to copper compared with reflowed Pb-5Sn joints.

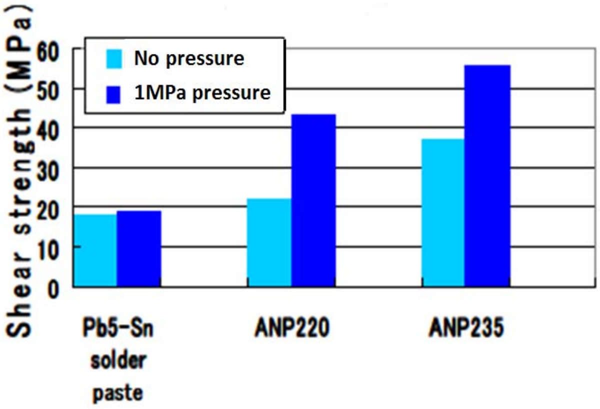


Figure 16. Shear strength of joint made to copper with nano silver solder paste with and without 1 MPa pressure compared with that of Pb-5Sn solder paste.

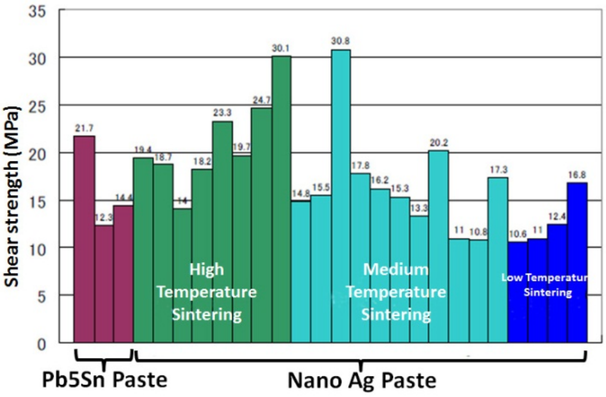


Figure 17. Shear strength of silver pastes sintered without pressure compared with reflowed Pb-5Sn solder paste.

APPLICATIONS OF NANO SILVER PASTE

In addition to die attach applications such as that described earlier in this paper alcoxide-passivated nano silver pastes can used to create printed wiring on substrates such as polyimide (Figure 18) and to be effective in wire bonding (Figure 19)

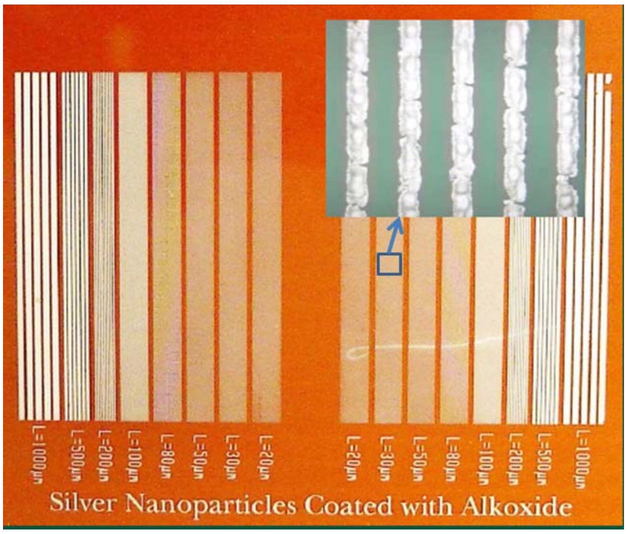


Figure 18. 20µm to 1000µm traces screen printed on polyamide with alcoxide-passivated nano silver paste sintered at 150C. Inset is 30µm traces

The alcoxide-passivated nano silver paste has been proven to have high bond strength to silver, gold, platinum, copper, iron and 304 stainless steel surfaces. The tenacious oxide films on nickel and aluminium interfere with the formation of the metal to metal bond by the highly active surface of the nano particles.

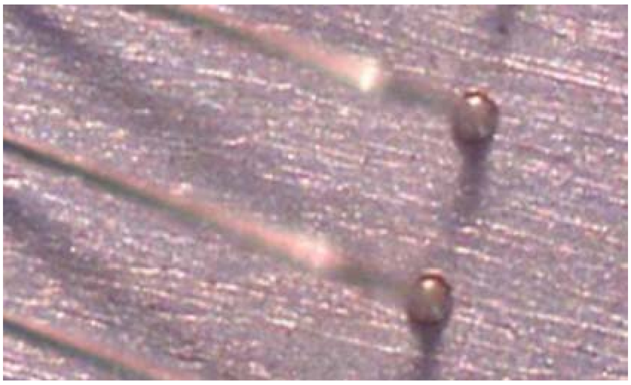


Figure 19. Wire bonding with alcoxide-passivated nano silver paste.

CONCLUSIONS

Sufficient evidence has been accumulated to prove that nano silver manufactured in an alcohol environment and passivated with alcoxides formed by reaction with the silver atoms on the surface of the particles can provide the basis for joining materials that can be sintered at temperature comparable with those used in the reflow of high-lead solder pastes and lower. The strength and electrical and thermal conductivity of the bond so formed is at least comparable with that formed by the reflow of high-lead solder

While the nano silver so formed can be used alone it has also been shown to be possible to reduce the cost of the material and enhance mechanical properties by mixing the nano particles with sub-micron particles of silver and copper.

The temperature required for sintering the nano silver paste varies with the length of the carbon chain of the alcohol used for its passivation with sintering temperatures under 120°C possible with nano silver passivated with alcohols with 2 to 6 carbon atoms although there is trade off in regard to stability. Selecting a nano silver paste formulation it is therefore a matter of choosing the balance between sintering temperature and storage and handling stability that best fits the application.

Figure 20. Examples of pastes based on alcoxide-stabilized nano-silver.

ACKNOWLEDGEMENTS

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